

## PERMIT APPLICATION INSTRUCTIONS FOR INDUSTRIAL SURFACE WATER EFFLUENT MONITORING REQUIREMENTS

All industrial permittees discharging to surface waters and applying for a permit reissuance must monitor the physical, chemical and biological characteristics of each outfall. The monitoring that each permittee must perform is based on the category of discharger and also on individual circumstances.

These instructions are provided to help you complete the tables used to characterize effluent quality. To help avoid problems, we suggest that you forward a copy of these instructions and any information on what calculated limits for any of the substances would be (if you know) to your laboratory.

### ➤ **What are my testing requirements?**

You must complete a set of tables for each outfall that discharges effluent to surface waters. Specifically:

- **Outfalls Solely Discharging Noncontact Cooling Water**  
You must complete Tables A-1 through A-5 for each outfall discharging solely noncontact cooling water. You must provide test results for the parameters listed in Table A-1 of the application and for any parameter listed in Tables 1 and 2 of these instructions that you believe may be present in the discharge from the outfall at a concentration of 10 µg/L or greater. You must also complete Tables A-2 through A-5.
- **Outfalls Discharging Process Wastewater from Secondary Industry**  
You must complete Tables B-1 through B-5 for each outfall discharging process wastewaters from a secondary industry (i.e., an industry that is not included in the industrial categories listed in Table 4 of these instructions), cooling water, or boiler blowdown. (Cooling water means water which has been used primarily for cooling but which may be contaminated with process waste or airborne material. Barometric condenser cooling water and cooling tower blowdown are examples.) You must provide test results for the parameters listed in Table B-1 of the application and for any parameter listed in Tables 1 and 2 of these instructions that you believe may be present in the discharge from the outfall at a concentration of 10 µg/L or greater. Note that multiple tests are required for some of the parameters listed in Table B-1. You must also complete Tables B-2 through b-5.
- **Outfall Discharging Process Wastewater from Primary Industry**  
You must complete Tables C-1 through C-4 for each outfall discharging process wastewater from a primary industry (i.e., an industry that is included in the industrial categories listed in Table 4 of these instructions). You must provide test results for the parameters listed in Table C-1 in the application (with the exceptions explained in the introduction to Table C-1). You must also provide results for any parameter listed in Tables 1 and 2 of these instructions, that you believe may be present in the discharge from

the outfall at a concentration of 10 µg/L or greater. Note that multiple tests are required for some of the parameters listed in Table C-1.

The Effluent Monitoring Form, Table C-1, is divided into groups of pollutants entitled Common Pollutants; Metals, Cyanide, Hardness and Phenols; Volatile Organics; Acid Extractable Compounds; Base/Neutral Compounds; Pesticides; and Dioxins and Furans. All primary industry process wastewater outfalls must be tested for the Common Pollutants group and Metals, Cyanide, Hardness and Phenols group. To see which of the remaining 5 groups you must test, determine your primary industrial category listed in Table 4 of these instructions and note which pollutant groups apply to your category (designated by "X's" in Table 4).

In Table C- 1 of the application, record the primary industrial category for the outfall and place check marks in the appropriate boxes to indicate which pollutant groups you must test. For example, if you operate a battery manufacturing facility, you need to test for all of the parameters listed in the Common Pollutants group, the Metals, Cyanide, Hardness and Phenols group, the Volatile Organics group and the Base/Neutral Compounds group. You are not required to test for parameters in the Acid Extractable Compounds group, Pesticides group or Dioxins and Furans group.

If you are required to test for the Dioxins and Furans group but the Effluent Monitoring Form, Table C- 1, in your application package does not list dioxin, furan and their congeners, contact the permit drafter who is identified in the cover letter that accompanied this application package.

You must also complete Tables C-2 through C-4.

### ➤ **Additional Things to Consider When Planning My Monitoring**

- Discharge Monitoring Report Data - If your current permit requires regular monitoring and reporting of any parameter for which the application requires testing, you need not retest the parameter nor resubmit the test results (see Discharge Monitoring Report (DMR) Information section of the instructions for more information).
- Past Monitoring Results - Any monitoring results collected within the last 5 years may be used toward the monitoring required by the application if the monitoring results are representative of the current discharge.
- Identical Outfalls - If you have two or more outfalls that discharge substantially identical wastewaters, you may request permission from the Department to sample and analyze only one of the outfalls. If your request is granted, on a separate sheet of paper attached to the completed application, identify which outfall you did test, and describe why the outfalls that you did not test are substantially identical to the outfall that you did test. Identify both outfalls at the top of the Effluent Characteristics page.
- Intake Testing - You are not required to submit results of "intake" testing, unless you wish to demonstrate your eligibility for a "net" effluent limitation for one or more pollutants. If you do submit results of intake testing, make a copy of the appropriate Tables A-1 through A-5, Tables B-1 through B-5 or Tables C-1 through C-4 and write "intake"

immediately after the outfall number of each page. Be sure to indicate if samples were collected before or after the point of source water treatment or addition of chemical additives.

➤ **How must I perform this testing?**

It is important that you provide the Department with quality monitoring data, since that data will be used to help determine what regulatory requirements we place in your reissued permit. The three important steps in the process of providing the data are sampling, laboratory testing and data reporting. (For more detailed guidance on steps to follow to accomplish the required monitoring, see the Monitoring Procedures Guidance, which is included as an attachment to these instructions.)

- **Sampling** - Data generated by your laboratory are only as good as the samples you collect. You must insure that the composition of your samples is as close as possible to the composition of the wastewater streams you are sampling. To do this you must consider sample time and location and you must minimize contamination. The time when you sample should be representative of your normal operation, to the extent feasible, with all processes which contribute wastewater in normal operation, and with your treatment system operating properly with no system upsets. Sample types, preservation methods and maximum holding times are listed in Table 1, provided in the Additional Information part of these instructions. Although Table 1 specifies 24-hour composite samples for many of the substances, the Department may waive composite sampling for any outfall for which you demonstrate that use of an automatic sampler is not feasible and that a minimum of four grab samples will be representative of the discharge from the outfall. Sample preservation must be performed immediately. Labs will need to check if samples arrived at the laboratory meeting temperature requirements.

If you are required to monitor for a parameter more than once, you must ensure a sufficient interval between discharge samples. If we have not specified a monitoring interval for a parameter, weekly intervals are generally about right. Please do not sample more frequently than once every 3 days unless we so direct you.

- **Laboratory Testing** - Sample analyses shall be performed by laboratories that are certified by the Department. You may contact the Laboratory Certification Program, WI DNR, 101 S. Webster St., Box 7921, Madison WI 53707, (608) 267-7633 for a current list of certified labs. Alternatively, visit the Program's World Wide Web Site at <http://www.dnr.state.wi.us/org/es/science/lc/search/>. Select a lab that can meet your needs for proper sensitivity and data quality.

We suggest that you provide a copy of the Effluent Monitoring Form, along with these instructions, to your laboratory. The Effluent Monitoring Form will tell your laboratory personnel what substances they need to test and the quality control information they need to supply with the data.

Unless instructed otherwise, you must use approved analytical test methods as identified in

ch. NR 219, Wisconsin Administrative Code. For many pollutants, more than one analytical test method is approved. Your lab should pay close attention to analytical detection limits in selecting the proper test methods and should use any available information that might help predict effluent limitations to guide them in this effort. Recognize that detection limits can be affected by analytical test methods and clean up procedures, interference or sample contamination.

The Department has listed recommended test methods in Table 1 in the Additional Information part of these instructions in an attempt to balance the need to measure compounds below levels that are environmentally significant against method sensitivity and positive compound identification. A number of the substances given in Table 1 are toxic in the environment at levels below the analytical detection limits of even the most sensitive analytical methods. If you report these substances as not detected and your lab did not use a method as sensitive as the one recommended in Table 1 or reports an unusually high detection limit above the Department's level of concern, the Department may require you to repeat the testing. However, you may be able to provide an explanation for the high detection limit and indicate those steps taken by your laboratory to lower the detection limit.

- **Data Reporting** - Report the data on the Effluent Monitoring Form (Tables A-1, B-1 or C-1) or the Additional Monitoring Form (Tables A-2, B-2 or C-2).

A numerical test result, by itself, is not very meaningful. The other information that you report on these forms will be used to help determine how accurately the data represents your discharge. It should also serve as a quality check for you. If you find that an unusual circumstance or qualifying information pertains to a certain piece of data, you should immediately take steps to clarify the situation, such as through re-sampling.

At your request, the Department can supply you with electronic copies of the Effluent Monitoring Form. It may make it easier for you to display the data. The Department has made electronic copies of the report form available to many commercial laboratories. Therefore, your contract lab may be able to produce a computer-generated analytical report identical to this form. In that case you may simply attach a copy of the lab's analytical report and save yourself the need to transcribe the data onto this paper form. We still recommend that you supply a copy of the Effluent Monitoring Form (along with any knowledge of potential limits) to your laboratory so they can provide you the most complete information.

➤ **Effluent Monitoring Form (Form A-1, B-1 and/or C-1)**

- **Blank Cells** - Please fill in all blank cells in the table. Where the cells have been pre-filled or shaded, you need not record any further information. You may use ditto marks or simply draw a vertical arrow down a column for entries that are the same on consecutive lines.
- **Outfall Number** - Please make sure the correct outfall number appears on each page of

the form.

- **Parameters** - You must monitor for each parameter in the table. The table is pre-printed with the parameters you must test and, when multiple samples are required, it contains the correct number of lines for the test results (i.e., one line for each required test result).
- **Additional Sample Results** - You may provide more sample results than specified by the table. For example, if your initial sample result for a substance is greater than 1/5 of your expected effluent limitation, or if you have some reason to think that the data you have is not representative of your discharge, you probably will want to sample at least several more times. To report that additional data, use the Additional Monitoring Form by filling in as many lines as there are sample results. If you need more lines than are on the sheet, please make photocopies of the blank form before you start.
- **Properly Collected and Representative Effluent Samples** - Indicate whether or not the effluent sample was properly preserved and handled and is representative of normal operating conditions. If not, the effluent must be re-sampled.
- **Lab Reports** - The information necessary to complete the form should be available to you on the analytical report(s) provided to you by your contract laboratory. Sometimes the Department finds it necessary to refer directly to the lab reports. Please attach copies of lab report for any monitoring not done to fulfill routine, permit-required effluent discharge monitoring.

#### Column by Column Instructions for Table A-1, B-1 and/or C-1

- **Parameter Code** - This is a unique number that normally will be pre-printed and is used as a reference by the Department.
- **Parameter Name** - The parameter name column will normally be pre-printed with the name of the substance for which you must report data. The CAS (Chemical Abstract Services) number for that parameter is also pre-printed on the form.
- **Sample Result** - Record the numerical result as provided to you by your laboratory. Make sure to report the correct results for the units reported. If a substance is not detected in a sample, report the result as < (less than) the value of the detection limit. For example, if the substance ammonia nitrogen is not detected and your laboratory indicates that the detection limit is 0.1 mg/L, report the result as <0.1 in the sample result cell.
- **QC Flags** - Use this column to signal that there has been some sort of laboratory quality control (QC) exceedance. The entry in this space should normally be a letter of the alphabet or some other common typographical symbol. Similar to how a footnote is used in text documents, explain the meaning of the "flag" at the bottom of the report form.

*(NOTE: Flagged data are not necessarily bad data. However, unless your laboratory has documentation, which shows that a quality control exceedance did*

*not affect sample results, please arrange for re-analysis or re-sampling and analysis for affected parameters.)*

- **Units** - The units column normally will be pre-printed with the units of measurement in which you should report the analytical results. If your laboratory reports results for a given substance in different units, you will need to convert them to the pre-printed units. Usually, a change in units requires that you move the decimal point 3 places to the right or left. For example, 0.018 mg/L is the same as 18 µg/L. 8 ng/L is the same as 0.008 µg/L. If you are unsure how to convert the results into the required units, contact the permit drafter who is identified in the cover letter that accompanied this application package.
- **Detection Limit (LOD)** - Record a numerical value for the limit of detection (LOD) reported to you by your laboratory. Sometimes this quantity is called to the method detection limit (MDL). You need not report a detection limit for substances when that space is shaded, such as for temperature or pH.
- **LOQ (Limit of Quantitation)** - Record the numerical value for the limit of quantitation (LOQ) reported to you by your laboratory. You need not report a limit of quantitation for certain substances, such as temperature or pH.
- **Analytical Method** - Record what laboratory analytical method was used to test for the substance. Usually, methods are usually specified using method numbers. Refer to Table 1 of these instructions for a listing of recommended analytical test methods.
- **Confirmed Organics (Y/N)** - For organic substances, if you report a detected result, indicate if a detected result has been confirmed. GC/MS methods do not require separate confirmation. If a GC/MS method was used to generate a detected result, enter Y (yes) in this column. If a GC method produced a detect, answer Y if the detect was confirmed and N (no) if it was not. You may need to consult with your laboratory if this information is not provided on the laboratory's report of analytical results.
- **Sample Collection Date** - Record the day, month and year (mm/dd/yy) when the sample was collected. If the sample is a 24-hour composite, please show the end date of the compositing period.
- **Extraction Date** - For organic substances, record the day, month and year (mm/dd/yy) when the sample was extracted in the laboratory.
- **Analysis Date** - Record the day, month and year (mm/dd/yy) when the sample was analyzed in the laboratory or in the field.
- **Lab ID Number** - Provide the nine-digit Wisconsin laboratory certification number of the lab that performed the analyses. If analytical testing was sub-contracted to another lab, you still must provide the certification number of the lab that performed the analyses.
- **Sample Type (Co/Gr)** - Record the type of sampling used for that parameter. ("Co"

means 24-hour composite sample. "Gr" means grab sample.) Table 1 of these instructions lists required sample types by parameter.

- **DMR (Discharge Monitoring Report)** - You do not have to retest those parameters that your WPDES discharge permit currently requires you to monitor, nor do you have to resubmit the monitoring data. Simply place a check mark (✓) in the DMR column for those parameters.

➤ **Additional Monitoring Form (Tables A-2, B-2 and/or C-2)**

- **Purpose of the Form** - This form should be used for two purposes, reporting analytical results when monitoring is performed more frequently than that required by the Effluent Monitoring Form and reporting analytical results for parameters from Tables 1 and 2 that you believe are present in the discharge from the outfall.
- **Reporting Additional Monitoring Results** - If you have sampled for a parameter more frequently than required by the Effluent Monitoring Form, please provide the extra test results on the Additional Monitoring Form. Copy the correct parameter code, name and units from the Effluent Monitoring Form and write this information in the correct columns on the Additional Monitoring Form. Use as many lines as there are results.
- **Additional Substances Believed Present In the Discharge** – If you know, or have reason to believe that any parameter listed in Tables 1 and 2 is present in the discharge from the outfall at a concentration greater than 10 µg/L, write the name of the parameter and its parameter code on the Additional Monitoring Form. This excludes those parameters for which you have already reported test results or for which you have checked the DMR column on the Effluent Monitoring Form. Provide at least one sample result for the parameter. Place a check mark in the Intake cell if you feel that the parameter is present in the discharge solely as a result of its presence in your intake water, OR place a check mark in the DMR cell if you have provided a sample result for the parameter on a recent Discharge Monitoring Report. If you provide a sample result for a parameter, also complete the remaining columns as instructed. Base your determination that a pollutant is believed present on your knowledge of your raw materials, maintenance chemicals used, intermediate and final products and byproducts, and any previous analyses known to you of your effluent or similar effluent. Indicate that you evaluated the presence of all parameters in Tables 1 and 2 by placing a check mark in the box at the beginning of Tables A-2, B-2 and/or C-2.
- **For Primary Industries Only** - For primary industry wastewaters, you may use the Effluent Monitoring Form, Table C-1 rather than the Additional Monitoring Form, Table C-2 to report test results for those parameters that you believe are present in the discharge, but were not required to test when completing the Effluent Monitoring Form.

➤ **Hazardous Substances Form (Tables A-3, B-3 and/or C-3)**

For each parameter listed in Table 3 of these instructions that you know or have reason to

believe is present in the discharge from the outfall, write the name of the parameter and its parameter code on the Hazardous Substances Form.

- Provide any monitoring data that you may have for the parameter, unless you have already provided that data on recent Discharge Monitoring Reports.
- Place a check mark in the DMR cell if you have provided monitoring data for the parameter on recent Discharge Monitoring Reports.
- Place a check mark in the Intake cell if you expect the parameter is present in the discharge solely as a result of its presence in your intake water, and explain why you believe the parameter is present in the discharge from the outfall. No analytical testing is required for Table 3 parameters.

➤ **Discharge Monitoring Report (DMR) Information (Tables A-4, B-4 and/or C-4)**

When evaluating effluent quality, the Department usually assumes that the information reported by the permittee on its Discharge Monitoring Reports (Forms 3200-28 and 3200-40) for the last 36 months is representative of the permittee's current discharge.

- If you agree that the last 36 months of DMR information accurately represents the current discharge from your outfall, place a check mark in the first box of the Discharge Monitoring Report Information table.
- If you believe that a time period other than the last 36 months is representative of the current discharge, check the second box in the table, specify the time period over which you believe DMR data are representative of the current discharge and provide the reasons for your belief. For example, a time period less than 36 months would be appropriate if 18 months ago you added or modified a production process or a wastewater treatment process.
- If you believe certain DMR data points over the selected time period are not representative of the current discharge, check the third box, identify the data points and provide the reasons for your belief.

➤ **Additives (Tables A-5 and/or B-5) (For Secondary & Noncontact Cooling Water Outfalls Only)**

- Tables A-5 and/or B-5 must be completed when the outfall discharge consists of noncontact cooling water, contact cooling water, cooling tower blowdown and/or boiler blowdown in the absence of other process wastewaters. Enter "NA" (i.e., not applicable) in the comment cell of the table and continue on to the next section of the application if the discharge contains process wastewaters other than noncontact cooling water, contact cooling water, cooling tower blowdown and/or boiler blowdown.
- For the purposes of this section, additives include all biocides and water quality conditioners that are added to cooling and boiler waters. Examples of water treatment additives include microbicides, fungicides, molluscicides, scale and corrosion inhibitors, pH adjustment chemicals, oxygen scavengers, water softening compounds, etc.
- For each additive, attach the following information to the completed application.



- ❑ Material Safety Data Sheets - Provide a Material Safety Data Sheet (MSDS) for each additive except chlorine, hypochlorite, bromine, sulfuric and hydrochloric acids, and sodium hydroxide. The MSDS should show the active chemical ingredients of the additive, the density of the additive if it is a liquid, and, if available, the aquatic toxicity of the additive.
  - ❑ Toxicity Data - Provide any aquatic life toxicity data that is available for each additive except chlorine, hypochlorite, bromine, sulfuric and hydrochloric acids, and sodium hydroxide. If aquatic toxicity data is not included on the MSDS, please contact the chemical supplier or manufacturer for this information. If at least one 48-hour LC50 or EC50 for *Daphnia magna* or *Ceriodaphnia dubia* and at least one 96-hour LC50 or EC50 for fathead minnow, rainbow trout or bluegill sunfish are not provided for each additive, the Department will likely include whole effluent toxicity testing requirements in the reissued permit.
- For each additive, provide the following information in Table A-5 and/or B-5.
    - ❑ Additive Name and Manufacturer - List the additive name and manufacturer.
    - ❑ Purpose of Additive - State the reason why you use the additive. For example, the additive is a biocide, it is used to prevent scale or adjust pH, it is used as a flocculent or water softening agent, etc.
    - ❑ Intermittent or Continuous Feed - Indicate whether the additive, when in use, is applied to the system continuously or intermittently. Intermittent feed is the periodic addition of the additive on a sporadic or timed basis, or based on the level of a water characteristic, such as the concentration of dissolved solids, within the system. Continuous feed is the uninterrupted addition of the additive to the system. Continuous feed is often used to maintain the concentration of the additive as a specific level within the system.
    - ❑ Frequency of Use - Indicate the number of months per year that the additive is used at least once. For example, if the additive is used at least once each month during the entire year, you would enter "12" in the "months per year" column. If the additive is used only during the summer months of May through September, you would enter "5".

On average over the period when the additive is in use, determine the number of days per week that the additive is applied to the system and enter the result in the "days per week" column. For example, if the additive is applied weekly over the summer months enter "1". If the additive is applied every third day over a period of six months, you would enter "2.3". (That is, 60 days of additive application divided by 180 days between the first and last day of additive application, times 7 days per week.)

- ❑ Maximum Quantity Used - Identify the maximum amount of additive, in pounds (lbs) or gallons (gal) per day that you intend to apply to the system during any one day.
- ❑ Average Quantity Used - Identify the average amount of additive, in pounds (lbs) or gallons (gal) per day that you intend to apply to the system over the period of additive use. For example, if 60 pounds of additive will be used over five months the average quantity used would be 0.4 pounds per day. (That is, 60 pounds divided by 150 days.)
- ❑ Concentration of Additive at the Outfall - When determining the need for an effluent

limitation for an additive, the Department will likely assume that the entire amount of additive that is applied to the system during a day will be present in the discharge from the system for that day. The Department will use the flow information that you provide in the Surface Water Outfall Location, Wastewater Sources and Treatment Technologies section of this application to perform this calculation. For example, if on average 10 pounds of an additive are applied to the system per day and the annual average discharge from the system is 10,000 gallons per day, the Department will assume the discharge contains 120 mg/L of additive. (That is, 10 pounds divided by the product of 0.01 million gallons of discharge per day times 8.34.)

If you believe that the above calculation misrepresents the actual concentration of the additive at the discharge outfall, enter the value, in parts per million (ppm), that you believe more accurately represents the discharge concentration and explain how you derived the value. You may use discharge-monitoring results if available for an additive. You may also estimate an additive's concentration at the outfall using stoichiometry and/or mass balance approaches.

## ADDITIONAL INFORMATION

### TABLE 1. - SAMPLING, PRESERVATION AND ANALYTICAL INFORMATION

#### Substances Which May Require Testing With Permit Applications

Parameter	Sample Type <sup>a</sup>	Recommended Analytical Test Methods <sup>b</sup>	Preservation <sup>c</sup>	Maximum Holding Time <sup>c</sup>
<u>COMMON POLLUTANTS</u>				
Biochemical Oxygen Demand (BOD <sub>5</sub> )	24-hr. comp.	-	Cool to 4 <sup>0</sup> C	48 hours
Chemical Oxygen Demand (COD)	24-hr. comp.	-	Cool to 4 <sup>0</sup> C	28 days
Chlorides, Total	24-hr. comp.	-	None require EPA 335.4ed	28 days
Chlorine, Total Residual	Grab	EPA 330.2 (amperometric), 330.5, or electrode	Analyze immediately	-
Nitrogen, Ammonia	24-hr. comp.	-	Cool to 4 <sup>0</sup> C, H <sub>2</sub> SO <sub>4</sub> to pH < 2	28 days
Oil and Grease	Grab	EPA 1664	Cool to 4 <sup>0</sup> C, pH to < 2	28 days
PH	Grab	-	Analyze immediately	-
Phosphorus, Total	24-hr. comp.	-	Cool to 4 <sup>0</sup> C, H <sub>2</sub> SO <sub>4</sub> to pH < 2	28 days
Suspended Solids, Total	24-hr. comp.	-	Cool to 4 <sup>0</sup> C	7 days
Temperature	Grab	-	Analyze in field	-
<u>METALS, CYANIDE HARDNESS AND PHENOLS</u>				
Antimony, Total Recoverable	24-hr. comp.	EPA 200.9 <sup>d</sup>	HNO <sub>3</sub> to pH < 2	6 months
Arsenic, Total Recoverable	24-hr. comp.	EPA 200.9 <sup>d</sup>	HNO <sub>3</sub> to pH < 2	6 months
Beryllium, Total Recoverable	24-hr. comp.	EPA 200.7 or 200.9 <sup>d</sup>	HNO <sub>3</sub> to pH < 2	6 months
Cadmium, Total Recoverable	24-hr. comp.	EPA 200.7 or 200.9 <sup>d</sup>	HNO <sub>3</sub> to pH < 2	6 months
Chromium, Hexavalent	Grab	EPA 218.6	Cool to 4 <sup>0</sup> C	24 hours
Chromium, Total Recoverable	24-hr. comp.	EPA 200.7 or 200.9 <sup>d</sup>	HNO <sub>3</sub> to pH < 2	6 months
Copper, Total Recoverable	24-hr. comp.	EPA 200.7 or 200.9 <sup>d</sup>	HNO <sub>3</sub> to pH < 2	6 months
Cyanide, Total	Grab	EPA 335.4	Cool to 4 <sup>0</sup> C, NaOH to pH > 12, neutralize Cl <sub>2</sub>	14 days
Cyanide, Amenable	Grab	EPA 335.1	Cool to 4 <sup>0</sup> C, NaOH to pH > 12, neutralize Cl <sub>2</sub>	14 days
Lead, Total Recoverable	24-hr. comp.	EPA 200.7 or 200.9 <sup>d</sup>	HNO <sub>3</sub> to pH < 2	6 months
Mercury, Total Recoverable	Grab <sup>e</sup>	EPA 1631E	See Method	90 days
Nickel, Total Recoverable	24-hr. comp.	EPA 200.7 or 200.9 <sup>d</sup>	HNO <sub>3</sub> to pH < 2	6 months
Selenium, Total Recoverable	24-hr. comp.	EPA 200.9 <sup>d</sup>	HNO <sub>3</sub> to pH < 2	6 months
Silver, Total Recoverable	24-hr. comp.	EPA 200.9 <sup>d</sup>	HNO <sub>3</sub> to pH < 2	6 months
Thallium, Total Recoverable	24-hr. comp.	EPA 200.7 or 200.9 <sup>d</sup>	HNO <sub>3</sub> to pH < 2	6 months
Zinc, Total Recoverable	24-hr. comp.	SW-846 7950 or EPA 200.7	HNO <sub>3</sub> to pH < 2	6 months
Hardness (Total as CaCO <sub>3</sub> )	24-hr. comp.	-	HNO <sub>3</sub> to pH < 2	6 months
Phenols, Total	24-hr. comp.	-	Cool to 4 <sup>0</sup> C, H <sub>2</sub> SO <sub>4</sub> to pH < 2	28 days
<u>VOLATILE ORGANICS</u>				
Acrolein	Grab	SW-846 8260B	Cool to 4 <sup>0</sup> C, neutralize Cl <sub>2</sub> , adj. pH to 4-5	14 days
Acrylonitrile	Grab	SW-846 8260B	Cool to 4 <sup>0</sup> C, neutralize Cl <sub>2</sub>	14 days
Benzene	Grab	SW-846 8260B	Cool to 4 <sup>0</sup> C, neutralize Cl <sub>2</sub> , HCl to pH < 2	14 days
Bromodichloromethane (dichlorobromo-methane)	Grab	SW-846 8260B	Cool to 4 <sup>0</sup> C, neutralize Cl <sub>2</sub>	14 days
Bromoform	Grab	SW-846 8260B	Cool to 4 <sup>0</sup> C, neutralize Cl <sub>2</sub>	14 days

Parameter	Sample Type <sup>a</sup>	Recommended Analytical Test Methods <sup>b</sup>	Preservation <sup>c</sup>	Maximum Holding Time <sup>c</sup>
Carbon tetrachloride	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
Chlorobenzene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub> , HCl to pH < 2	14 days
Chlorodibromo-methane (dibromochloromethane)	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
Chloroethane	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
Chloroform	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
Chloromethane (methyl chloride)	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
1,2-Dichlorobenzene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub> , HCl to pH < 2	14 days
1,3-Dichlorobenzene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub> , HCl to pH < 2	14 days
1,4-Dichlorobenzene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub> , HCl to pH < 2	14 days
1,1-Dichloroethane	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
1,2-Dichloroethane	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
1,1-Dichloroethylene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
<i>cis</i> -1,2 Dichloroethylene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
<i>trans</i> -1,2-Dichloroethylene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
1,2-Dichloropropane	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
1,3-Dichloropropane	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
1,1-Dichloropropylene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
<i>cis</i> -1,3-Dichloropropylene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
<i>trans</i> -1,3-Dichloropropylene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
2,3-Dichloropropylene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
Ethylbenzene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub> , HCl to pH < 2	14 days
Methyl bromide (bromomethane)	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
Methylene chloride (dichloromethane)	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
1,1,2,2-Tetrachloroethane	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
Tetrachloroethylene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
Toluene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub> , HCl to pH < 2	14 days
1,1,1-Trichloroethane	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
1,1,2-Trichloroethane	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
Trichloroethylene	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
Vinyl Chloride	Grab	SW-846 8260B	Cool to 4°C, neutralize Cl <sub>2</sub>	14 days
<b>ACID EXTRACTABLE COMPOUNDS (Phenols)</b>				
2-Chlorophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
3-Chlorophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
4-Chlorophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
2-Chloro-5-methylphenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
2,3-Dichlorophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
2,4-Dichlorophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
2,5-Dichlorophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>

Parameter	Sample Type <sup>a</sup>	Recommended Analytical Test Methods <sup>b</sup>	Preservation <sup>c</sup>	Maximum Holding Time <sup>c</sup>
2,6-Dichlorophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
3,4-Dichlorophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
2,4-Dimethylphenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
2,4-Dinitrophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
2,5-Dinitrophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
2-Methyl-4-chlorophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
3-Methyl-4-chlorophenol ( <i>para</i> -chloro- <i>meta</i> -cresol)	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
2-Methyl-4,6-dinitrophenol (4,6-dinitro- <i>ortho</i> -cresol)	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
2-Nitrophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
4-Nitrophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Pentachlorophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Phenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
2,3,4,6-Tetrachlorophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
2,4,5-Trichlorophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
2,4,6-Trichlorophenol	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
<b>BASE/NEUTRAL COMPOUNDS</b>				
Acenaphthene	24-hr. comp.	SW-846 8270C or 8310	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Acenaphthylene	24-hr. comp.	SW-846 8270C or 8310	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Benidine	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Bis(2-chloroethoxy) methane	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Bis(2-chloroethyl) ether	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Bis(2-chloroisopropyl) ether	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Bis(2-ethylhexyl) phthalate	24-hr. comp.	SW-846 8270C	Cool to 4°C	7 days <sup>f</sup>
4-Bromophenyl-phenyl ether	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Butyl benzyl phthalate	24-hr. comp.	SW-846 8270C	Cool to 4°C	7 days <sup>f</sup>
2-Chloronaphthalene	24-hr. comp.	SW-846 8270C	Cool to 4°C	7 days <sup>f</sup>
4-Chlorophenyl-phenyl ether	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
3,3'-Dichlorobenzidine	24-hr. comp.	SW-846 8270C	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Diethyl phthalate	24-hr. comp.	SW-846 8270C	Cool to 4°C	7 days <sup>f</sup>
Dimethyl phthalate	24-hr. comp.	SW-846 8270C	Cool to 4°C	7 days <sup>f</sup>
Di- <i>n</i> -butyl phthalate	24-hr. comp.	SW-846 8270C	Cool to 4°C	7 days <sup>f</sup>
2,4-Dinitrotoluene	24-hr. comp.	SW-846 8270C	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
2,6-Dinitrotoluene	24-hr. comp.	SW-846 8270C	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Di- <i>n</i> -octyl phthalate	24-hr. comp.	SW-846 8270C	Cool to 4°C	7 days <sup>f</sup>
1,2-Diphenylhydrazine	24-hr. comp.	SW-846 8270C	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Hexachloroethane	24-hr. comp.	SW-846 8270C	Cool to 4°C	7 days <sup>f</sup>
Isophorone	24-hr. comp.	SW-846 8270C	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
N-Nitrosodi- <i>n</i> -butylamine	24-hr. comp.	SW-846 8270C	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
N-Nitrosodiethylamine	24-hr. comp.	SW-846 8270C	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
N-Nitrosodimethylamine	24-hr. comp.	SW-846 8270C	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>

Parameter	Sample Type <sup>a</sup>	Recommended Analytical Test Methods <sup>b</sup>	Preservation <sup>c</sup>	Maximum Holding Time <sup>c</sup>
N-Nitrosodiphenylamine	24-hr. comp.	SW-846 8270C	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
N-Nitrosodi- <i>n</i> -propylamine	24-hr. comp.	SW-846 8270C	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
N-Nitrosopyrrolidine	24-hr. comp.	SW-846 8270C	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Naphthalene	24-hr. comp.	SW-846 8270C	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Nitrobenzene	24-hr. comp.	SW-846 8270C	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
1,2,4-Trichlorobenzene	24-hr. comp.	SW-846 8270C	Cool to 4°C	7 days <sup>f</sup>
<u>Chlorinated Hydrocarbons Requiring Specialized Testing</u>				
Hexachlorobenzene	24-hr. comp.	SW-846 8121 (GC)	Cool to 4°C	7 days <sup>f</sup>
Hexachlorobutadiene	24-hr. comp.	SW-846 8121 (GC)	Cool to 4°C	7 days <sup>f</sup>
Hexachlorocyclopentadiene	24-hr. comp.	SW-846 8121 (GC)	Cool to 4°C	7 days <sup>f</sup>
Pentachlorobenzene	24-hr. comp.	SW-846 8121 (GC)	Cool to 4°C	7 days
1,2,4,5-Tetrachlorobenzene	24-hr. comp.	SW-846 8121 (GC)	Cool to 4°C	7 days <sup>f</sup>
<u>Polynuclear Aromatic Hydrocarbons Requiring Specialized Testing</u>				
Anthracene	24-hr. comp.	SW-846 8310 (HPLC)	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Benzo( <i>a</i> )anthracene	24-hr. comp.	SW-846 8310 (HPLC)	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Benzo( <i>a</i> )pyrene	24-hr. comp.	SW-846 8310 (HPLC)	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Benzo( <i>b</i> )fluoranthene	24-hr. comp.	SW-846 8310 (HPLC)	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Benzo( <i>ghi</i> )perylene	24-hr. comp.	SW-846 8310 (HPLC)	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Benzo( <i>k</i> )fluoranthene	24-hr. comp.	SW-846 8310 (HPLC)	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Chrysene	24-hr. comp.	SW-846 8310 (HPLC)	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Dibenzo( <i>a,h</i> )anthracene	24-hr. comp.	SW-846 8310 (HPLC)	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Fluoranthene	24-hr. comp.	SW-846 8310 (HPLC)	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Fluorene	24-hr. comp.	SW-846 8310 (HPLC)	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Indeno(1,2,3- <i>cd</i> )pyrene	24-hr. comp.	SW-846 8310 (HPLC)	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
Phenanthrene	24-hr. comp.	SW-846 8310 (HPLC)	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days
Pyrene	24-hr. comp.	SW-846 8310 (HPLC)	Cool to 4°C, Store in the dark, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>
<u>PESTICIDES</u>				
Aldrin	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
<i>alpha</i> -BHC ( - hexachlorocyclohexane)	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
<i>beta</i> -BHC ( - hexachlorocyclohexane)	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
<i>delta</i> -BHC ( - hexachlorocyclohexane)	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
<i>gamma</i> -BHC ( - hexachlorocyclohexane, Lindane)	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
Chlordane	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
4,4'-DDT	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
4,4'-DDE	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
4,4'-DDD	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
Dieldrin	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
<i>alpha</i> -Endosulfan	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
<i>beta</i> -Endosulfan	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
Endosulfan sulfate	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
Endrin	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>

Parameter	Sample Type <sup>a</sup>	Recommended Analytical Test Methods <sup>b</sup>	Preservation <sup>c</sup>	Maximum Holding Time <sup>c</sup>
Endrin aldehyde	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
Heptachlor	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
Heptachlor epoxide	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
Toxaphene	24-hr. comp.	SW-846 8081A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
Chlorpyrifos	24-hr. comp.	SW-846 8141A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
Parathion, (ethyl)	24-hr. comp.	SW-846 8141A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
Parathion, (methyl)	24-hr. comp.	SW-846 8141A	Cool to 4°C, pH 5-9	7 days <sup>f</sup>
PCB-1016	24-hr. comp.	SW-846 8082	Cool to 4°C	7 days <sup>f</sup>
PCB-1221	24-hr. comp.	SW-846 8082	Cool to 4°C	7 days <sup>f</sup>
PCB-1232	24-hr. comp.	SW-846 8082	Cool to 4°C	7 days <sup>f</sup>
PCB-1242	24-hr. comp.	SW-846 8082	Cool to 4°C	7 days <sup>f</sup>
PCB-1248	24-hr. comp.	SW-846 8082	Cool to 4°C	7 days <sup>f</sup>
PCB-1254	24-hr. comp.	SW-846 8082	Cool to 4°C	7 days <sup>f</sup>
PCB-1260	24-hr. comp.	SW-846 8082	Cool to 4°C	7 days <sup>f</sup>
<b>DIOXINS AND FURANS</b>				
All dioxin and furan congeners including 2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin (TCDD) and 2,3,7,8-Tetrachloro-dibenzofuran (TCDF)	24-hr. comp.	EPA 1613 <sup>g</sup>	Cool to 4°C, neutralize Cl <sub>2</sub>	7 days <sup>f</sup>

### Notes on Table 1:

<sup>a</sup> Grab sample means a single sample taken at one moment of time or a combination of several smaller samples of equal volume taken in less than a 2 minute period. Where the term is used in connection with monitoring temperature or pH it means a single measurement.

24 hour composite sample means a combination of individual samples taken at intervals of not more than one hour such that the volumes of each of the individual samples and of the combination are proportional to the volumes of flow during each interval and during the 24 hour period respectively.

<sup>b</sup> Each method recommendation assumes a commonly achievable sensitivity and the strictest regulatory level. If the recommended method, or one which is comparably sensitive, is used with reasonable care, a "not detected" result is generally considered sufficient demonstration of a pollutant's absence, even if the detection limit is above the regulatory level. Any other approved method may be used for analyses if sample results are comfortably in the range of quantitation of the method or if the method's detection limit is below the regulatory level. However, if a result from a less sensitive method is reported as "not detected" and the level of detection is above the regulatory level, the Department may require the permittee to repeat the analysis using the more sensitive method. If there is no recommended method listed, any method approved in s. NR 219, Wisconsin Administrative Code may be used.

If preliminary limits are included with the permit application, the permittee, in conjunction with their lab, may use these limits to help decide if methods other than those recommended may be used (and to decide if additional sample results should be collected). If preliminary limits have not been provided for any substance, please use the recommended (or comparably sensitive) method. If a recommended method is not listed, any approved method in Chapter NR 219, Wis. Adm. Code, may be used.

For many of the most toxic of the metals, we have listed inductively coupled plasma atomic emission spectrometry (ICP) as well as graphite furnace atomic absorption spectrometry (GFAA) because many labs report ICP sensitivities that rival those of GFAA. Labs should use preliminary limits to help decide which method is most appropriate for the required sensitivity.

We have avoided recommending the older EPA metals methods from Chemical Analysis of Water and Wastes, first published in 1979 with several subsequent versions. We anticipate these methods will be de-commissioned. Instead, we have recommended the methods from Methods for the Determination of Metals in Environmental Samples, 1991 (first version). Note that, the ICP method in this more recent version, specifies use of CAL solutions with concentrations toward the lower end of the linear range.

For metals sample preparation (digestion), the older methods distinguished between "total" and "total recoverable" metals, while the newer versions drop the total designation. While the older definitions and methods are still listed in NR 219, we wish to move to the convention of only using the total recoverable designation and urge use of the total recoverable digestion detailed in method 200.2 from Methods for the Determination of Metals in Environmental Samples.

<sup>c</sup> See NR 219, Table F and associated footnotes for further details on sample preservation and holding times.

<sup>d</sup> Standard Methods 3113B may be substituted for EPA's AA furnace method.

<sup>e</sup> NR 106.145 requires that permittees perform field blanks and other data quality steps. We strongly recommend that any permittee that uses surface water as its water supply source performs side-by-side intake or background surface water monitoring whenever performing effluent testing for mercury.

At this time, the following list of laboratories are certified or registered to perform the low-level mercury testing. Method 1631 is performance-based (permittees and labs may use alternative procedures so long as those procedures are demonstrated to yield reliable results at the levels of interest). The Department recognizes the capabilities of these labs to perform this low-level work because they have documented use of appropriate quality control steps for the level of sensitivity stated. The Department has asked these labs to prepare special sampling instructions aimed at minimizing sample contamination for this low-level work.

Facility sampling personnel should closely follow the instructions provided by their lab.

Commercial Labs

Battelle Marine Sciences, Sequim, Washington (Telephone (360) 683-4151).

Brooks-Rand, Washington (Telephone (206) 632-6206)

En Chem, Inc., Madison, Wisconsin (Telephone (608)232-3300.

Frontier GeoSciences, Seattle, Washington (Telephone (206) 622-6960).

Northern Lake Service, Crandon, Wisconsin (Telephone (715) 478-2777, contact Mal Gross).

S-F Analytical, Milwaukee, Wisconsin (Telephone (414) 473-6700).

Other Recognized Labs

Green Bay Metropolitan Sewerage District, Green Bay, Wisconsin (Telephone (920) 432-4893).

Madison Metropolitan Sewerage District, Madison, Wisconsin (Telephone (608) 222-1201).

Wisconsin State Laboratory of Hygiene, Madison, Wisconsin (Telephone (800) 442-4618).

Vulcan Chemicals (registered), Port Edwards, Wisconsin (Telephone (715)887-4541.

Wisconsin Electric Power Company, Milwaukee, Wisconsin (Telephone (414)221-2345.

<sup>f</sup> The holding time is 7 days prior to extraction, 40 days after extraction.

<sup>g</sup> EPA Method 1613 or Appendix C in the 5 Mill Study (EPA 440/1-88-025), March 1988.



**TABLE 2. - PARAMETERS REQUIRED TO BE TESTED IF BELIEVED PRESENT**  
**(Use Additional Monitoring Form)**

Parameter#	Parameter Name (CAS#)	Parameter#	Parameter Name	Parameter#	Parameter Name
	Bromide (24959-67-9)		Radioactivity, Alpha, Total		Aluminum, Total Recoverable (7429-90-5)
	Color		Radioactivity, Beta, Total		Barium, Total Recoverable (7440-39-3)
	Fecal Coliform		Radioactivity, Radium, Total		Boron, Total Recoverable (7440-42-8)
	Fluoride (16984-48-8)		Radioactivity, Radium 226		Cobalt, Total Recoverable (7440-48-4)
	Nitrate plus Nitrite Nitrogen (as N)		Sulfate (as SO <sub>4</sub> ) (14808-79-8)		Iron, Total Recoverable (7439-89-6)
	Nitrogen, Total Organic (as N)		Sulfide (as S)		Magnesium, Total Recoverable (7439-95-4)
			Sulfite (as SO <sub>3</sub> ) (14265-45-3)		Manganese, Total Recoverable (7439-96-5)
			Surfactants		Molybdenum, Total Recoverable (7439-98-7)
					Tin, Total Recoverable (7440-31-5)
					Titanium, Total Recoverable (7440-32-6)

**TABLE 3. - TOXIC POLLUTANTS AND HAZARDOUS SUBSTANCES TO BE IDENTIFIED**  
**(if Believed Present)**  
**(Use with Hazardous Substances Form)**

Asbestos	Dimethyl amine	Nitrotoluene
Acetaldehyde	Dinitrobenzene	Parathion
Allyl alcohol	Diquat	Phenolsulfonate
Allyl chloride	Disulfoton	Phosgene
Amyl acetate	Diuron	Propargite
Aniline	Epichlorohydrin	Propylene oxide
Benzonitrile	Ethion	Pyrethrins
Benzyl chloride	Ethylene diamine	Quinoline
Butyl acetate	Ethylene dibromide	Resorcinol
Butylamine	Formaldehyde	Strontium
Captan	Furfural	Strychnine
Carbaryl	Guthion	Styrene
Carbofuran	Isoprene	2,4,5-T (2,4,5-Trichloro- phenoxy acetic acid)
Carbon disulfide	Isopropanolamine	TDE (Tetrachloro- Diphenylethane)
Chlorpyrifos	Dodecylbenzenesulfonate	2,4,5-TP [2-(2,4,5-Trichloro- phenoxy) propanoic acid]
Coumaphos	Kelthane	Trichlorofan
Cresol	Kepone	Triethanolamine dodecyl- Benzenesulfonate
Crotonaldehyde	Malathion	Triethylamine
Cyclohexane	Mercaptodimethur	Trimethylamine
2,4-D (2,4-Dichlorophenoxy acetic acid)	Methoxychlor	Uranium
Diazinon	Methyl mercaptan	Vanadium
Dicamba	Methyl methacrylate	Vinyl acetate
Dichlobenil	Methyl parathion	Xylene
Dichlone	Mevinphos	Xylenol
2,2-Dichloropropionic acid	Mexacarbate	Zirconium
Dichlorvos	Monoethyl amine	
Diethyl amine	Monomethyl amine	
	Naled	
	Napthenic acid	

**TABLE 4 - PRIMARY INDUSTRIES AND POLLUTANT GROUPS REQUIRING TESTING**

INDUSTRIAL CATEGORY	POLLUTANT GROUPS				
	Volatile Organics	Acid Extractable Compounds	Base/Neutral Compounds	Pesticides	Dioxins and Furans
Adhesives and sealants	X	X	X		
Aluminum forming	X	X	X		
Auto and other laundries	X	X	X	X	
Battery manufacturing	X		X		
Coal mining	X	X	X	X	
Coil coating	X	X	X		
Copper forming	X	X	X		
Electric and electronic compounds	X	X	X	X	
Electroplating	X	X	X		
Explosives manufacturing	X	X	X		
Foundries	X	X	X		
Gum and wood chemicals					
All subparts except D and F	X	X			
Subpart D	X	X	X		
Subpart F	X	X	X		
Inorganic chemicals manufacturing	X	X	X		
Iron and steel manufacturing	X	X	X		
Leather tanning and finishing	X	X	X		X
Mechanical products manufacturing	X	X	X		
Nonferrous metals manufacturing	X	X	X	X	
Ore mining (applies to Subpart B)		X			
Organic chemicals manufacturing	X	X	X	X	X
Paint and ink forming	X	X	X		
Pesticides	X	X	X	X	
Petroleum refining	X				X
Pharmaceutical preparations	X	X	X		
Photographic equipment and supplies	X	X	X		
Plastic and synthetic materials manufacturing	X	X	X	X	
Plastic processing	X				
Porcelain enameling					
Printing and publishing	X	X	X	X	
Pulp, paper and paperboard mills					
Subpart A - Dissolving Kraft	X	X			X

INDUSTRIAL CATEGORY	POLLUTANT GROUPS				
	Volatile Organics	Acid Extractable Compounds	Base/Neutral Compounds	Pesticides	Dioxins and Furans
Subpart B - Bleached Papergrade Kraft and Soda	X	X			X
Subpart C - Unbleached Kraft		X		X	X
Subpart D - Dissolving Sulfite	X	X			X
Subpart E - Papergrade Sulfite	X	X	X		X
Subpart F - Semi-chemical		X			X
Subpart G - Mechanical Pulp	X	X			X
Subpart H - Non-Wood Chemical Pulp	?	?	?	?	X
Subpart I - Secondary Fiber Deink	X	X		X	X
Subpart J - Secondary Fiber Non-Deink	X	X		X	X
Subpart K - Fine and Lightweight Papers from Purchased Pulp					
Nonintegrated Fine		X			X
Nonintegrated Lightweight	X	X		X	X
Subpart L - Tissue, Filter, Non-Woven and Paperboard from Purchased Pulp	X	X		X	X
Rubber processing	X	X	X		
Soap and detergent manufacturing	X	X	X		
Steam electric power plants	X	X			
Textile mills (excluding Subpart C)	X	X	X		
Timber products processing	X	X	X	X	

## MONITORING PROCEDURES GUIDANCE

*A generalized procedure for obtaining chemical specific monitoring data follows. Use it to tailor your own procedure.*

- A. Review specific requirements of permit or application request.
- B. Hire a certified laboratory. Supply your laboratory with appropriate parts of your permit application, including the Effluent Monitoring Form, preliminary limits, if included in the application package, and associated instructions.
- C. Decide when to sample.
  - 1. Industrial discharges should be at normal to maximum levels, usually this means mid-week but avoid always sampling on the same day(s) of the week.
  - 2. The treatment plant should be operating normally.
  - 3. If unusual circumstances occur just before or during sampling, stop and start over after the situation has stabilized.
  - 4. Consider sample holding times and lab workload when scheduling sampling events. Consult your laboratory prior to initiating sampling to make sure that the dates you select do not conflict with the laboratory's scheduling.
  - 5. Consider sample transportation and laboratory arrival times.
- D. Determine proper sample location.
  - 1. The proper location is the plant effluent after all unit processes.
  - 2. Chlorination/dechlorination processes may affect samples for various substances. Keep this in mind if disinfection processes are in operation when sampling is performed. For example, if you need to sample for cyanide amenable to chlorination and you chlorinate seasonally, collect the grab sample prior to chlorination. Also, as indicated in Table 1, the presence of chlorine also affects sample preservation requirements for certain substances.
  - 3. The effluent stream should be well mixed at the point of sampling.
- E. Prepare for sampling.
  - 1. Obtain sample containers and proper preservation chemicals. (These items should be obtained from your laboratory.)
  - 2. Prepare equipment; clean sampler(s). If using an automatic sampler, adhere to sampler cleaning requirements given below. For "flow through" samplers, careful cleaning and acclimation to the wastewater may be appropriate.
  - 3. Coordinate routine testing to help serve as a measure of plant performance.
  - 4. Contact your laboratory again to make sure they are ready for your samples.
- F. Collect samples.
  - 1. Grab samples -- Collect according to precautions and preserve. (If doing composite sampling for other parameters, the grab samples should be taken during the composite sampling.)
  - 2. Composite sampling: NR 218 requires that composite samples be **flow-proportional**

G. Ship samples to a certified laboratory (most laboratory chain of custody forms should contain this information).

1. Ship with ice or refrigeration to maintain 4°C. If ice packs are used or if ice is not in direct contact with the sample containers, include a 250 ml. or larger temperature blank with the samples.
2. Make sure all sample containers are clearly marked with contents, including preservatives.
3. Enclose information regarding the exact date(s) and time(s) of sampling.
4. Remember sample holding time limits.

H. When data comes back from the laboratory, report data to the Department.

1. Check data for errors. Does it look reasonable?
2. Assemble all information, including remarks on sampling and analysis.
3. Fill in all blanks on the Effluent Data Reporting Form(s)

### **Cleaning Automatic Samplers**

Special provisions should be considered if using automatic samplers to collect composite samples for priority pollutant analysis. The following cleaning procedures have been suggested for suction/tubing type samplers. Alternately, consider replacing tubing and cleaning before use.

A. Pump Tubing and Line Hose Cleaning

1. Rinse by pumping hot water through the tubing for at least 2 minutes.
2. Acid rinse the tubing by pumping 20 percent hydrochloric acid or 20 percent nitric acid through the tubing for at least 2 minutes. The acid rinse should be recirculated. The acid rinse may be reused up to 4 times.
3. Repeat Step 1.
4. Rinse by pumping distilled water through the hose for at least 1 minute. After 1 minute, stop the pump and allow water to stand in the hose for at least 1 minute. After 1 minute, continue pumping rinse water for 1 additional minute. The distilled rinse should not be recirculated.
5. For priority pollutants (organics and trace metals), the hose should be flushed with pesticide grade or redistilled acetone, then rinsed again with distilled water. (Note: hose must be Teflon for organics).
6. Beware of possible zinc contamination with silicon pump tubing.

B. Sampler Cleaning - General Washing

1. Flush assembled sampler (manual or automatic) with tap water.
2. Disassemble, submerge and/or rigorously scrub all parts, which contact the sample with hot tap water and a non-phosphorus detergent.
3. Rinse and drain all items three times with tap water, and then follow with three distilled water rinses.

**NOTE:** Sampler bottles can be glass or polyethylene for metals, but only glass for organics. Use glass sampler bottles if sampling for metals and organics simultaneously.